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Further Development of Processes for the Conversion of Wood to Liquid Fuels through the Operation of a Continuous/Semi-Continuous Liquefaction Unit

by

D.G.B. Boocock and D. Mackay

Contractor's Final Report [1]
DSS Contract 24SU.KN107-2-4069

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ABSTRACT

A laboratory scale continuous/semi-continuous wood liquefaction unit, which was constructed under a three-year ENFOR contract (C-44), has been modified and evaluated further. The unit consists of a 2-L stirred tank (high pressure) reactor. An aqueous slurry of powdered wood and nickel carbonate is fed via a tubular lock system. High pressure water displaces the slurry into the reactor. Product discharge is via a dip tube to a cooled lock system from where it is discharged to a separation vessel.

The reactor inlet was modified by Autoclave Engineering to alleviate plugging problems, and the dip tube for product collection was extended. Heated and cooled sections on the feed line have been used to minimise leaks (due to thermal shock) and valve seat failure. The modified system does not plug when 10 per cent slurries of less than 60 mesh wood are used. It has been identified that the actual operation of the unit requires several personnel for safe and smooth operation. Carbon balances on the unit have been achieved and 2 runs have been carried out for the International Energy Agency Program (Biomass Liquefaction Test Facility).

In related studies, not directly funded by this contract, it has been found that chip-sized wood can be liquefied when heated rapidly to 350°C in water.

PREAMBLE

The work performed under this contract related to the operation and evaluation of a laboratory-scale continuous/semi-continuous wood liquefaction unit in which wood is liquefied catalytically. Related work on the direct liquefaction of wood by rapid heating to 350°C in the presence of water has also continued and the major findings of this study will be communicated in a separate report.

PERSONNEL

Mr. Asad Chowdhury has carried the major responsibility for the maintenance, modification, and operation of the wood liquefaction unit. However, toward the end of the contract Mr. Edmundo Vasquez, a Ph.D. student embarking on coal liquefaction studies in this Department, gave valuable assistance. In addition it was identified near the end of this contract that, if data was to be collected in a safe manner over a period of hours, then several personnel were required. In this regard, three graduate students, Mr. Foster Agblevor, Mr. David Chow, and Mr. Frank Porretta gave valuable assistance.

We again thank Dr. Ralph Overend, the Scientific Authority on this contract.

INTRODUCTION

The work performed under this contract was under a 1 year extension of ENFOR contract - Development of a Process for Conversion of Wood into Liquid Fuel (ENFOR Contract C-44, DSS 05SS.KL-9-7053).

The major objective of the work performed under the original contract, was to take the existing knowledge on catalytic wood liquefaction gained from batch studies, and design and construct a small-scale (ca 2 L capacity) continuous system capable of wood conversion at a rate of 0.2 kg/h. The system was to be tested using prolonged continuous runs, thus generating data essential for the design of larger scale pilot plants.

The key problem in the design of the system was that of feeding, from atmospheric pressure, a wood/water slurry to a system containing a pressure equivalent to the vapour pressure of water at 350°C plus pressures due to reactant or product gases. A similar problem existed for removing products from the reactor. A secondary consideration was the rate of feed which would be necessary to satisfy the optimum residence time of the wood. This latter parameter was not available, since data at the start of this project had been obtained in batch autoclaves in which heat-up times to 350°C were usually no less than one hour. If the optimum residence time were very short, then the addition of fresh, cold feed would place a large thermal load on the reactor, even if the feed were preheated to some extent. In the absence of this important information, it was decided that the reactor itself would be a 2-L vessel of the same type used in our batch runs and that the system would be designed to allow feeding and discharging, while the autoclave was

operating. A choice had to be made on the type of feed system either a discontinuous lock system or a continuous system. A truly continuous system might consist of a screw feeder, the rate of feed being controlled by the rotation of the screw. However, at the start of the project this type of feed system was still not fully evaluated, and we were hesitant to adopt it. We therefore chose a lock system.

In the lock system, slurry in the lock is displaced by clean water into the reactor. After the slurry has cleared the lock the valves are operated so that the water is in turn displaced by the next slurry charge. The volume of the lock, the rate of feed from the lock and the number of feed cycles together control the thermal load on the reactor. It was anticipated that the lock would be sufficiently large that a slow feed rate would be normal, with infrequent cycles. With rapid lock recharging, the operation would be almost continuous. A similar system, but using a second autoclave rather than a lock, was used by Osterman for kinetic studies on cellulose liquefaction (this unit was not continuous).

A lock system was also chosen for the product let-down and collection system.

STATUS AND OPERATION OF UNIT AS OF MARCH 31, 1982

A schematic diagram of the unit as it existed as of April 1982 is shown in Figure 1, and photographs are included in the main copy of this report for reference.

The unit is based on a 2-L Autoclave Engineering packless Magnedrive-stirred autoclave. The only modification ordered was the

facility for a bottom feed. We considered that the head of the autoclave was too crowded to accommodate a feed line of sufficient diameter.

The lock itself is a piece of high pressure tubing (internal diameter 1.3 cm) rated at 30 MPa (4500 psi max) and having a volume of about 325 mL. The original intention was to place sight glasses at either end to allow observation of the discharging and recharging of the system. However, the pressure specifications on available sight glasses made their use dubious from the safety aspect, and thus it was decided that the valve timings for charge and discharge would have to be determined by experiments. Ultra-sound and radioactive detectors for wood/water systems have been investigated, but no suitable detector has yet been found. The lock system is controlled by four half inch stainless steel ball valves. Originally these were to be manually operated, but since the opening and closing of these valves is critical, particularly the sequencing, it was decided, in consultation with the Scientific Authority, that these valves should be remotely operated through Marpac air operated drivers. Electronic interlocks insured that it would not be possible to inadvertantly vent the vessel and the valves were fail safe, closing to the normally closed position, in the event of air line failure. The catalytic process uses a hydrogen atmosphere and the original intention was to provide high pressure hydrogen using an available gear pump and high pressure reservoir and not purchase a

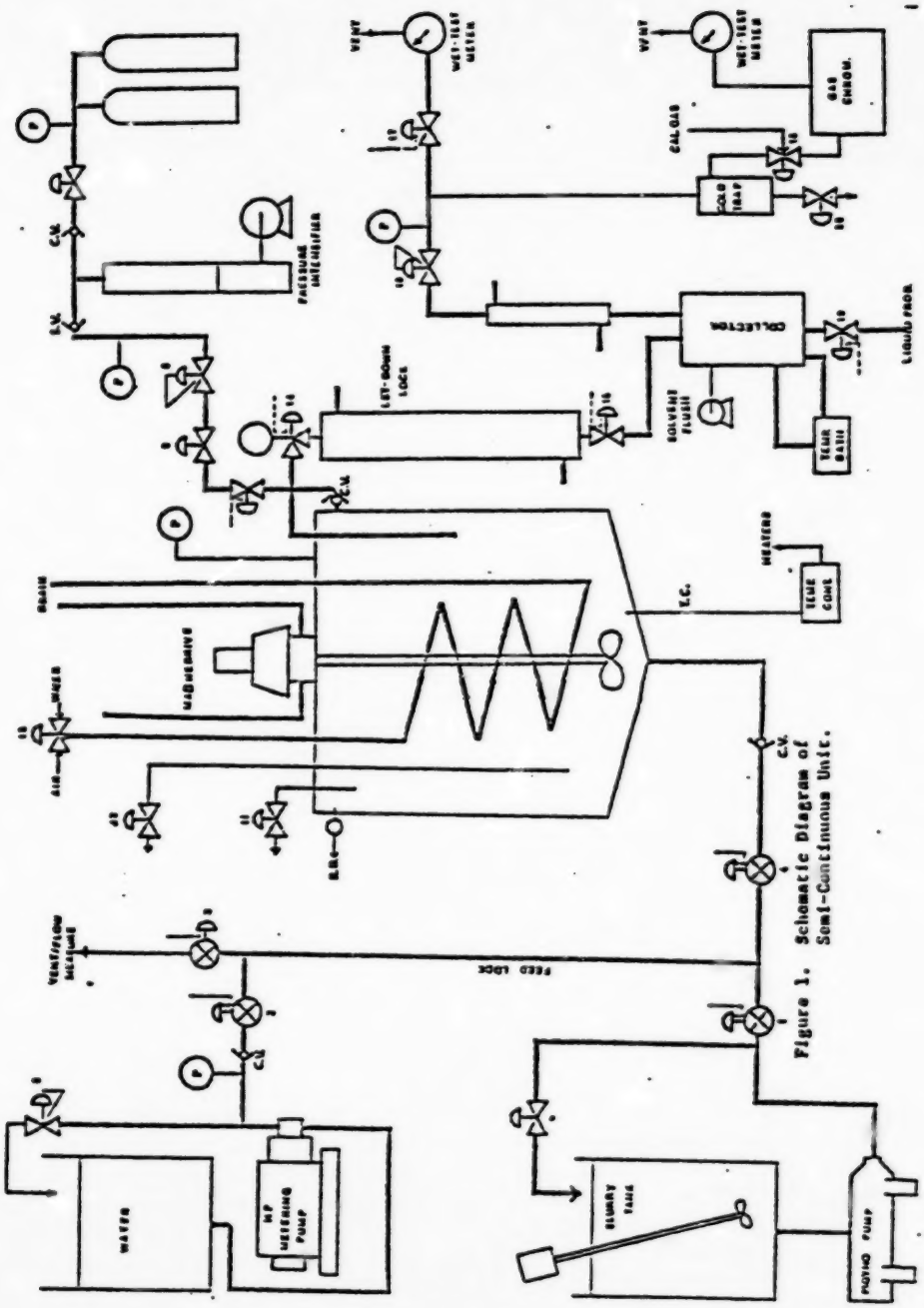


Figure 1. Schematic Diagram of Semi-Continuous Unit.

hydrogen compressor at this time. However, it was believed that the gear pump would be unable to supply sufficient hydrogen. Fortunately a temporary solution has been found. High pressure hydrogen cylinders, as supplied to us, contain a pressure of 26.7 MPa (4000 psi) compared to the expected 23.3 MPa (3500 psi). Thus we have been skimming these cylinders, and this will continue until the system is truly proved, at which time it will be decided if a more advanced system is required.

The slurry feed system consists of a stirred slurry tank from which slurry is fed to a plastic recycle line which leaves the base of the tank, passes to and from the base of the lock and then discharges into the top of the slurry tank. The slurry feed is tapped from the recycle line. The height of the discharge line back into the tank helps control the filling of the lock in that the slurry rises in the lock, passes beyond the top valve and is prevented from rising further, since it is now at the same height as the discharge line. This prevents excessive discharge of slurry to waste.

MODE OF OPERATION OF UNIT

1. Charging

A filling sequence for the continuous unit consists of the following (it is assumed that the autoclave is at a temperature of 350°C):

(a) With the slurry in the tank stirring, and the slurry recycle line in operation, driven by a Robbins and Myers Moyno pump, the lock is filled by opening valves 1 and 2 (see schematic diagram). The slurry passes beyond valve 2 where it stops, due to the limit in pressure head

controlled by the discharge return to the slurry tank. Because of the surge, a small amount goes to waste together with the water which is displaced from the lock.

(b) The low pressure filling and vent valves (1 and 2) are closed, and a high pressure hydraulic (water) line valve (3) is opened. Hydraulic pressure is generated using a Milton-Roy Milroyal Model A metering pump. Pressure in the lock system is controlled by a Tescom back pressure regulator. On the condition that lock pressure is higher than the reactor pressure, the reactor inlet valve (4) is opened, and the feed hydraulically pumped into the reactor. High pressure feed rate is controlled and measured using a stroke length adjuster and electronic stroke counter on the metering pump.

(c) When the lock has nearly emptied, the reactor inlet valve is closed, and the vent valve opened to bring the lock to atmospheric pressure ready for the next cycle.

(d) Hydrogen gas as required is fed to the reactor headspace from cylinders through a Tescom high pressure regulator and check and surge valves.

Towards the end of the original contract, the slurry recycle loop was provided with a water flush system. This was necessary because the slurry in the recycle line settled when recycling was terminated, and this led to blocking of the recycle loop.

Clearances have been left for the incorporation of preheaters. The feed line has a cooling jacket which could also be used in a heating capacity.

2. Product Collection

Hot product leaves the reactor via a 3/8" dip tube. Entry into a primary let down lock is controlled by a remotely air operated Autoclave Engineering 3/8" medium pressure valve. The lock consists of 1" Autoclave Engineering tubing and fittings which are cooled by water flowing through an external copper jacket. Pressure and temperature in the lock are monitored. Exit from the lock is controlled by a valve, similar to the lock inlet valve, and can be controlled manually or (as planned) automatically by a pressure switch. Product (liquid and gases) flow to a separation vessel. Gas is vented through a regulator and volume measured by water displacement from a collection vessel. Gas analysis is performed using a Hewlett Packard HP 5880A with a dual column system and thermal conductivity detectors. Liquid is collected from the bottom of the separation vessel and can be further processed by centrifugation phase separation and distillation. Solvent flush can be used for periodic removal of residuals from the collection vessel.

STATUS OF EQUIPMENT (APRIL 1982) AND INITIAL MODIFICATIONS

As of April 1982 four problems were identified in the unit. One of these fell into the maintenance category in that the magnedrive unit required a complete overhaul. The most serious operational problem was plugging of the slurry which occurred at the base of the reactor and, to a lesser extent, at the last valve before the reactor inlet. The plugging at the reactor inlet was due to a reduction in the feed line diameter at the feed line/reactor adaptor (from 1.3 cm to 0.8 cm). The plug remained intact at a pressure differential of 23.3 MPa (4000 psi). These two problems were solved by returning the autoclave and magnedrive to Autoclave Engineering in Erie, Pennsylvannia, where the magnedrive was overhauled.

The diameter of the hole in the base of the reactor was also increased. This allowed the use of a simple inlet adaptor such that there was no decrease in the internal diameter of the feed line where it entered the reactor. Unfortunately this modification took about 16 weeks to complete, whereas we had been informed by Autoclave Engineering that only 2-3 weeks were required. The dip tube was extended by our own machine shop.

The reactor was received from Autoclave Engineering in August 1982. Since then 11 runs have been completed, and the information from these has brought the procedure to a point where at least carbon balances can be obtained on the system.

The first step was determination of the volumes of various sections of the system. Three significant values are (a) the volume of the lock (325 mL); (b) the volume of the let down lock (125 mL); and (c) the

volume between the last valve and the reactor inlet (70 mL). It was also determined that at a 3.3 MPa (500 psi) differential the high pressure water pump set at 70 per cent of capacity delivered 8 mL/s of pure water. Initial leak tests indicated that the packing on valve 4 (the valve before the reactor inlet) was defective. Also the lower adaptor of the dip tube was leaking as was the hydrogen inlet to the reactor. All these problems were rectified, whereupon a guage mounted on valve 5 (let down inlet) showed increased pressure indicating an internal leak in this valve. On inspection the V-shaped head of the valve stem appeared badly damaged. The valve was replaced.

Five series of mini-runs were made during late October and early November. A 10:1 water/wood slurry (5:1 wood/Nickel Carbonate) was used, and the reactor was initially pressurised with 2 MPa (300 psi) of hydrogen. At this time the whole inlet line was wrapped with heating tape with a thermocouple measuring the external wall temperature 10 cm below the reactor inlet. With this temperature at 120°C (by normal conduction it was about 90°C), and the reactor at 350°C, charging of slurry was made for 10 s. A burst of steam momentarily appeared from the inlet fitting. The unit operated for 3 h, and only one other burst of steam was noted in this time. In the next run using the same temperatures leaks at the inlet fitting were common. A typical temperature drop from 100°C to 70°C (at the point measured by the thermocouple) would cause leaks. (N.B. The leak at the inlet fitting is due to thermal shock. Very recent runs show that, if the outer wall temperature of the lagged fitting drops about 10°C below the reactor temperature, then the fitting will probably leak).

The unit was operated early in November for 3 h without serious problems. In the period November 10 to December 5, the main temperature controller ceased to operate and was replaced by an on-off proportional controller. Leaks were also encountered at the magnedrive connection to the autoclave and at valves 3 and 4. The internal seal (downstream) on valve 4 was damaged, certainly due to excessive heat conduction from the reactor and preheater. The seal was replaced, and a copper cooling coil, extending 15 cm (6") towards the reactor, was placed around the feed line.

SIGNIFICANT TEST RUNS

February 14, 1983

The unit was charged with slurry (60 mesh wood) as described previously and kept at 350°C for 1 h before the first let down. The let down line blocked, and the run was terminated (this was the first of two such occurrences). Heavy oil and char were found inside the reactor.

March 1, 1983

Slurry (800 mL) was charged as previously to the reactor (liquid level 25 mm above dip tube). The unit was operated continuously for 7 h without facing any major problems. This was the first long run which was terminated voluntarily. It was established that charging for 10-12 s (high pressure water pump set at 70% of maximum stroke) and discharging for 4 s seemed to be a reasonable mode of operation.

March 8, 1983

Wood of less than 40 mesh was charged. After one hour of operation, there was an emergency shut down of the central compressed air supply (this is used to operate the valves). After resumption (about 1 h) the run was continued, but after 2 h the let down line blocked again. After termination of the run, the let down line was cleaned. A tape heater was placed around the body of the lower valve of the let down lock to keep the temperature at 45-50°C. It was also decided that warm water rather than cold water should be passed through the jacket of the lock.

March 15, 1983

The 40 mesh slurry was used in this run. The unit was operated for 2.5 h , whereupon it was noticed that the temperature inside the reactor was no longer dropping when fresh feed was supposedly being added. Eventually, only gas discharged from the let down system indicating that the liquid level had fallen below the dip-tube.

When the reactor was opened, the following observations were made:
(1) Heavy oil was deposited on the inner surface of the reactor, and the stirrer impeller blades. Heavy oil was also deposited inside the feed line at a point 5 cm below the heating tape.
(2) Wood particles were blocking valve #4 (15 cm before inlet side and 7.5 cm beyond outlet side).

March 22, 1983

This was performed in the same way as the previous run, and again blocking occurred at valve #4. In addition, the seat on the upstream

side of valve #4 was deformed. It appeared that wood particles had jammed behind the seat causing deformation as the ball returned to the closed position. It was decided that in all future runs wood less than 60 mesh (0.42 mm mesh) in size would be used. Wood of this size has not presented any plugging problems. At this time a gas collection system was set up. This consists of a 13 L glass vessel in which the gas downwardly displaces water, the volume of which is measured. When nearly all the water is displaced a gas sample is taken for analysis by gas chromatography.

April 7, 1983

Slurry was charged to the reactor as previously, i.e., 800 mL 10% slurry of IEA standard poplar (less than 60 mesh) in water containing 5% nickel carbonate. The head space, after flushing was charged with 2 MPa (300 psi) of hydrogen and the reactor brought to 350°C. All beneficial modifications made as the result of previous runs were incorporated in this run resulting in 6½ hours of uninterrupted operation. The following difficulties were encountered:

(a) The temperature controller seems to be of such a design that good temperature control is impossible without continuous manual adjustment of the set point. A BETTER (AND PRESUMABLY MORE EXPENSIVE) CONTROLLER IS REQUIRED. However, it was possible to keep the reactor temperature within ±7°C of the desirable set point of 350°C using the manual adjustment from time to time.

(b) Gas analysis could not be carried out in this run because the gas chromatograph was temporarily out of order.

(c) About half way through the 6½ hour period, the gas let down volume, which averaged about 1 L per let down, suddenly increased to about 4 L indicating that the liquid level had dropped below the inlet of the dip tube.

To compensate for this the charge time was increased from 12 s to 24 s. This caused the internal pressure to increase to 20 MPa (3000 psi) towards the end of the reaction presumably because the volume of the head space was decreased. As was discovered later, this pressure increase is also due to accumulation of methane and carbon dioxide in the head space.

(d) There was still no accurate way of determining the volume of hydrogen fed to the reactor. Generally 2 or 3 additions of hydrogen (2 MPa increase at reaction pressure) were made during the run.

(e) It was also realised that water balances would be virtually impossible. The feed rate was not accurately known. Also some slurry feed became diluted in backflushing the lock; i.e., the high pressure water stream partially dilutes the feed. This overflow was periodically returned to the slurry tank and more dry wood was later added to the tank to compensate for the dilution.

After the end of the run, the reactor was opened. Unlike some previous runs oil was not found sticking on the inner surface of the autoclave or to the impeller blades. Also there was no sign of any blocking of the inlet line. Some char was observed in the reactor, but oil was found preferentially in the let down system. All these preliminary runs

culminated in the first International Energy Agency run which was made on April 14, 1983, and is reported here in some detail. Personnel assisting in this run were Asad Chowdhury, D. Boocock, D. Chow, F. Porretta, F. Agblevor, and E. Vasquez.

IEA Test Run April, 14, 1983

The reactor was charged as follows:

WOOD TYPE: Poplar Clone DN-38 (less than 60 mesh)

CATALYST: Nickel Carbonate

WOOD:WATER MASS RATIO: 1:10

WOOD:CATALYST RATIO: 5:1

TOTAL RUN TIME: 8h 10m.

Wood (800 g), nickel carbonate (160 g) were added to distilled water (8.00 L) and thoroughly mixed in the feed tank on the morning of the run. Some of the slurry (800 mL) was removed and together with further nickel carbonate (50 g) was added to the clean autoclave through the dip tube port. The reactor was pressurised to 2.7 MPa (400 psi) with hydrogen (equivalent to 40 L at STP) which was more than sufficient to reduce the nickel carbonate in the reactor. Six thermocouples were used to monitor key temperatures (6 position switch on control panel). These were:

1. Interior reactor temperature.
2. External temperature of feed adaptor where it joins autoclave.

3. Feed line external temperature (10 cm below inlet).
4. Temperature of point between #4 valve cooling coil and inlet line heating tape.
5. External temperature of valve #4 outlet.
6. External temperature of valve #6 (let down lock outlet).

The reactor was heated to 350°C. The lock was kept empty during the heat up period to prevent slurry settling.

The sequence used was as follows:

A four second let down was made into the let down lock. Reactor temperature and pressures were noted before and after let down. The complete lock system was filled from the recirculating slurry line. The high pressure water pump was set to provide about 4 MPa (600 psi) higher pressure than the reactor. Initially a feed time of 18 s was used. Care was taken to keep the inlet fitting temperature (external) close to the reactor temperature. The reactor was charged about 80 times during the whole operation corresponding to a charge every 6 minutes. The actual time was slightly less since there was a break in the run while the inlet fitting was re-wrapped with heating tape. The delay between charges is limited by the time taken for the reactor and/or the inlet fitting to return to suitable temperatures.

After a feed had been made the cooled material in the lock was discharged into the glass separation vessel. The gas immediately passed to the water reservoir and the displaced water volume was measured. Throughout the run, the volume of the vented gas was measured and analysed. Aqueous phase and oil were collected from the let down vessel. Oil clinging to the wall of this vessel could be removed by slightly

heating the vessel so the oil flowed. In this way most of the oil could be separated from the aqueous phase. Some oil remaining in the water phase could be separated by cooling. Again towards the end of the run, the gas removed in a single let down increased dramatically. It was decided that the run would be terminated at this point because of the uncertainty in the liquid level. With the knowledge we now have the run would have been extended by increasing the ratio of feed cycles to let down cycles.

Throughout the run considerable attention had to be paid to the temperature controller and manual adjustment to the set point were made quite frequently. A chart recorder was set up to continuously monitor the external temperature of the inlet fitting. As feed was charged two cooling phases of this surface were evident. First a relatively slow cooling of about 10°C occurred followed (if feeding continued) by a steep temperature decline. If the temperature profile entered this second phase, the inlet fitting usually leaked.

When the reactor was opened it was noted that the liquid level in the reactor was below the dip tube. No oil was found sticking to reactor surfaces or propeller blades.

The following data were obtained for the feed and product components:

Components	Mass (g)	[a] % H_2O	[b] % C	[b] % H	% O	[b] % N	[b] % ash
Wood Feed < 60 mesh	1000	5.65 [c] 4.42	46.20 [c] 44.52	5.86 [c] 5.15	[d] 47.32 [c] 49.82	- [c] <0.04%	0.62 [c] 0.435
Nickel Carbonate Feed	250						
Wood and Nickel Carbonate Recovered	563	11.5					
Char	80	-	9.46				
Oil [e]	112	7.2	69.59	6.98	[d] 21.81 15.27 (maf)	0.39	1.62
Aqueous Phase Organics (Ether Extractable)	48		63.59	7.03			no ash
Gas (see separate table)							

a Moisture content determined by this laboratory (Karl-Fischer and oven drying) unless otherwise indicated.
b Analysis on undried sample by Schwarzkopf Microanalytical unless otherwise indicated.
c Data provided by Forintek (via D. Beckman)
d By difference - includes moisture oxygen.
e Phase separated plus acetone solubles.

We were supplied analytical data on the IEA poplar but no indication was given on how the analysis was performed. However, inspection of the figures indicates that the C, H, N and ash figures are not on a moisture-free basis. The oxygen figure appears to be calculated by difference and would thus include moisture oxygen. If so, then these figures are directly comparable with ours. It should be pointed out that single

analytical figures are not a good indicator of the macro elemental component of the feed. Ideally a macro analysis should be done on the feed.

Gas Composition (Volume %)

Component	Discharged During Run (91 L) 1	2	3	4	5	6	From Autoclave(101 L) 7a	7b
CO_2	92.4	91.2	93.0	92.2	93.0	91.6	74.9	68.7
CH_4	4.8	6.1	5.2	6.1	5.4	6.4	20.3	26.6
C_2H_6	0.87	1.1	0.87	0.83	0.86	1.0	2.8	3.0
C_2H_4	8.0×10^{-3}	5.0×10^{-3}	2.0×10^{-3}	NIL	NIL	NIL	NIL	NIL
C_3H_6	1.6	1.3	0.84	0.72	0.70	1.4	1.95	1.7
C_3H_6	0.64	0.22	0.06	0.14	NIL	NIL	NIL	NIL
CO	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL

Gas Products Weights

Component	During Run* (g)	From Autoclave** (g)
CO_2	165	142
CH_4	3.7	17.0
C_2H_6	1.1	3.9
C_2H_4	0	---
C_3H_8	1.9	3.6
C_3H_6	0.3	---

*Obtained using average gas composition for samples 1-6
**Obtained using average gas composition for samples 7a + 7b

Mass and Element Balances

The design of the equipment allows some mixing of the high pressure pure water and the slurry. Thus, the exact quantity of water fed to the reactor is unknown and a mass balance, which includes water, is impossible.

Our approach was to first examine the carbon balance and then look at the mass and oxygen balances excluding water. If the carbon balance is reasonable then one might expect that any deficiency in the oxygen balance might be reflected in a deficiency in the mass balance.

In calculating the balances it was assumed, because of the low solubility of nickel carbonate (0.009 g L^{-1}), that the ratio of wood and nickel carbonate in the unused feed was the same as at the start of the run.

Carbon

Input (g C)		Output (g C)	
Wood	440	Oil	78
$NiCO_3$	17	Gas	114
	457	Recovered Wood	193
		Recovered $NiCO_3$	8
		Aqueous Phase Organics	30
		Char	8
			431 (94.3% of Feed)

Mass Balance (Ex H_2O)

Input	Mass (g)	Output	Mass (g)
Wood (maf)	944	Oil (maf)	104
Nickel Carbonate	250	Char	80
Hydrogen	5	Gas	310
	1199	Recovered Wood	414
		Recovered Nickel Carbonate	83
		Aqueous Phase Organics	47
	(86.7% of Input)		1038

Oxygen Balance (Ex H_2O and $NiCO_3$)

Input	Mass oxygen (g)	Output	(mass oxygen g)
Wood	433	Oil	17
		Recovered Wood	190
		CO_2 other than from $NiCO_3$	197
		Aqueous Organics	15
		(96.7% of feed)	419

DISCUSSION

It is evident from the results obtained so far, particularly from the first IEA run, that the wood is undergoing aqueous pyrolytic liquefaction rather then catalytic liquefaction. The feed is brought to the reaction temperature so rapidly that there is insufficient time for intervention of nickel metal. In addition it is believed that the nickel carbonate which is introduced with the wood feed while the run is in progress is pyrolysed to nickel oxide which is then resistent to further reduction. Porretta of this group has already shown that when aqueous nickel carbonate is heated rapidly to 350°C in the absence of hydrogen the stoichiometric amount of carbon dioxide is produced. Beckman and Sherman of this group have shown that when powdered wood in water is heated rapidly to 350°C in small batch reactors initial high mass yields of oil are produced (45% containing 20-25% oxygen). However, yields drop quickly on increasing the residence time and mass yields of 19% with oil oxygen contents of 14% (m.a.f.) are consistent with the unvoidable long residence times in the unit. In contrast, batch catalytic (nickel carbonate/hydrogen) liquefaction with initial slow heat up gives 30-35% yields over fairly long residence times.

The carbon balance based on the total slurry available is close to 5%. However based on only the wood and nickel carbonate fed to the reactor the carbon deficiency is about 10%. The total mass balance, excluding water, is about 13% out and it was hoped that this might be mirrored in the oxygen mass balance (excluding water and nickel carbonate) and that the missing mass would be water. However, the oxygen

mass balance was very close. It is hoped that in future runs we will be able to place more reliance on element and mass balances.

Finally it should be emphasised that a large quantity of carbon dioxide is produced from the wood, 39% of wood carbon appearing in this form. Consideration of the total gaseous products shows that 46% of the wood carbon is contained in it. Preliminary results from a second IEA run in which nickel carbonate and hydrogen were not used indicate that less gas is produced from wood under these conditions and that product carbon monoxide is not shifted rapidly to carbon dioxide.

FUTURE PLANS

In the 1983/84 ENFOR contract the unit will be operated in the pyrolytic mode since the catalytic system is ineffective. Toward the end of that contract the future of the unit will be evaluated with the Scientific Authority.

LITERATURE

K.M. Sherman, Studies on the Rapid Hydropyrolysis of Poplar Wood M.A.Sc. Thesis, University of Toronto, 1983.

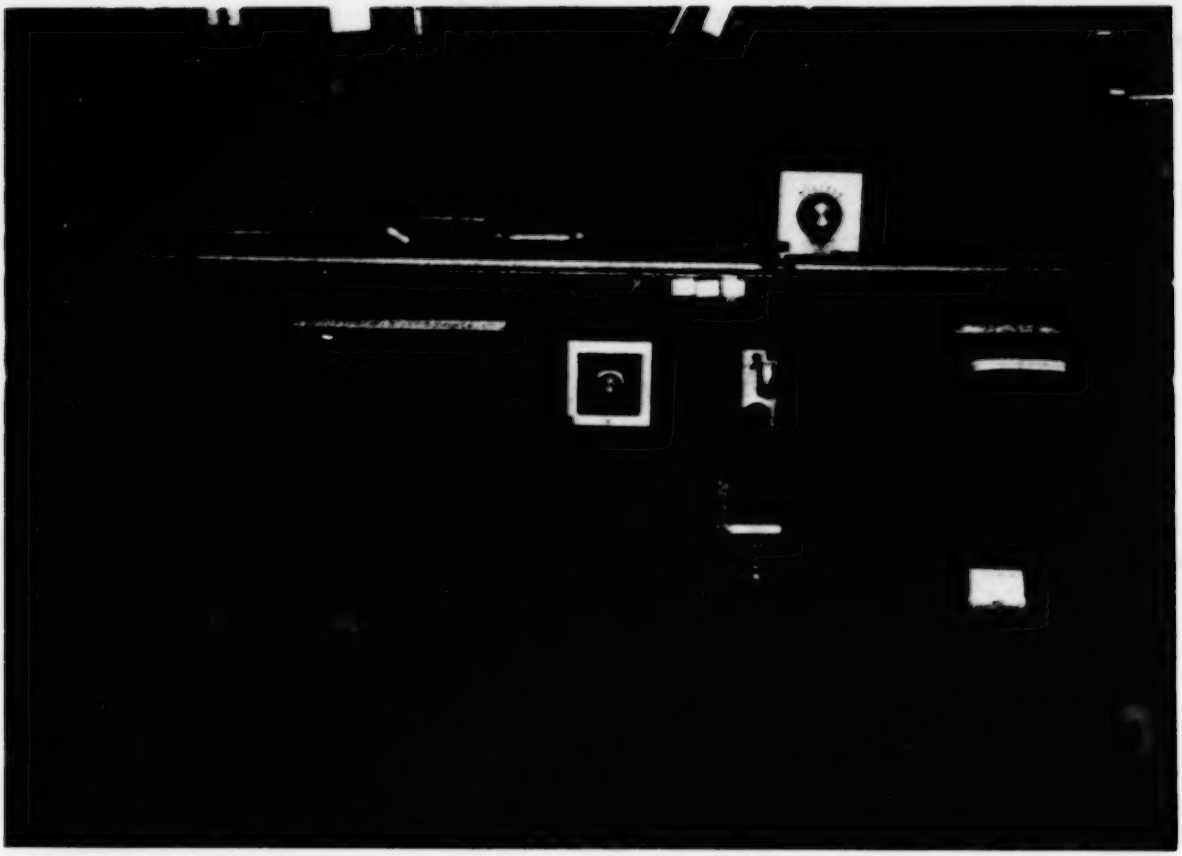
D. Beckman and D.G.B. Boocock, Liquefaction of Wood by Rapid Hydropyrolsis. Can. J. Chem. Eng., 61 80-85 (1981).

D. Beckman, Effects of Rapid Heat up on the Liquefaction of Wood, M.A.Sc. Thesis, University of Toronto, 1983.

F. Porretta, unpublished results.

WOOD LIQUEFACTION REACTOR

SLURRY FEED TANK



REACTOR CONTROL PANEL

POOR

QUALITY

ORIGINAL